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14. ABSTRACT Graphite nanoplatelets (GNPs) are an attractive class of reinforcement materials as they offer both high modulus and high strength. GNPs have a thickness of less than 100 nm although their planar dimensions can be as large as a few micrometers. As with any other nanoscale particles, their effectiveness as a reinforcement phase depends on the surface functionalization, which controls dispersion and interfacial bonding. A simple surface oxidation using nitric acid is shown to yield as good an improvement in composite properties as a few other functional groups chemically bonded to the surface do. The properties discussed include modulus, strength, fracture toughness, adhesive strength, thermal and electrical conductivities, and dielectric constants. Methods of further exfoliating graphite nanoplatelets are discussed together with the associated benefits on composite properties. Potential applications of graphite nanoplatelet composites are presented to conclude the report.					
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## Introduction

Carbon materials are widely used in various forms, such as fibers and flakes, as reinforcements and additives to improve properties of polymers. The use of carbon fiber composites in 50% of Boeing 787's structural weight is a crowning achievement of composites research over the past 5 decades. During the last decade new forms of carbon have become available, including carbon nanotubes, carbon nanofibers and graphite nanoplatelets (GNPs). Much research has been done on carbon nanotubes to fully exploit their excellent properties in structural composites. However, expected benefits still appear to remain somewhat elusive.<sup>1</sup>

Some of the properties which make carbon materials attractive are their high stiffness and strength, high electrical and thermal conductivities, and chemical inertness, while being lightweight.<sup>2,3</sup> One of the new promising carbon reinforcements is graphite nanoplatelet.<sup>4, 5, 6, 7, 8</sup> A graphite nanoplatelet consists of fewer than 300 graphene layers bound by weak van der Waals forces with their planar dimensions ranging from a micrometer to a few micrometers. Full exfoliation of micron-size graphite nanoplatelets can thus result in individual graphene sheets with a large aspect ratio easily exceeding 1000.

The benefits of 2-dimensional reinforcements via exfoliation have been demonstrated by organoclay nanoplatelets.<sup>9, 10</sup> Compared with clay, graphite has much more attractive properties in many aspects while they both share the same layered structure. Therefore, given proper functionalization, graphite nanoplatelets are expected to yield much better reinforcement effects.

The effect of reinforcement morphology on composite modulus is shown in Table 1, which follows from a simplified mechanics analysis under the assumption of high aspect ratio and high modulus ratio. When the reinforcements are randomly distributed in a 3-dimensional space, the plate geometry yields 3 times as high an improvement in modulus as the fiber geometry does.

Table 1. Approximate ratios of composite modulus to matrix modulus

	1-D Aligned	2-D Random	3-D Random
Particle	N/A	N/A	$1 + 3V_r$
Fiber	$1 + V_r \frac{E_r}{E_m}$	$1 + \frac{1}{3} V_r \frac{E_r}{E_m}$	$1 + \frac{1}{6} V_r \frac{E_r}{E_m}$
Platelet	$1 + V_r \frac{E_r}{E_m}$	$1 + V_r \frac{E_r}{E_m}$	$1 + \frac{1}{2} V_r \frac{E_r}{E_m}$

$V_r$  : reinforcement volume fraction     $E_r$  : modulus of reinforcement

$E_m$  : modulus of matrix

Assumptions:

Large aspect ratio

Large modulus ratio,  $E_r/E_m \gg 1$

Low reinforcement volume fraction,  $V_r \ll 1$

The full utilization of nanoscale reinforcements is contingent upon uniform dispersion of reinforcement phase and good interfacial bonding between the reinforcements and the matrix. To improve interfacial bonding, a number of methods are used to treat the surface of carbon fibers.<sup>2</sup> Lately, much more work has been done on functionalizing carbon nanotubes and nanofibers.<sup>11, 12, 13</sup> One facile method of functionalization is oxidation with nitric acid treatment. The nitric acid oxidation leaves the carboxyl group, among other oxygenated groups such as ketone, alcohol and ester groups, on the surface that can improve interfacial bonding to the surrounding matrix. A variety of other functional groups can also be attached to the GNP via the carboxyl group. Furthermore, when an amine curing agent is used, the carboxyl group on GNP can react with the amino group on the curing agent, thereby forming an amide linkage. The resulting chemical bonding between GNPs and the amine-cured epoxy resin yields excellent properties for the resulting composite.

The present chapter shows that a good quality GNP/epoxy composite can be produced by a combination of proper nitric acid treatment and intense sonication. The importance of processing sequence and surface functionalization is demonstrated using amine- and epoxy-functionalized GNPs. A significant amount of strength improvement is shown to be possible through prolonged sonication.

## **Materials**

### *Graphite Nanoplatelets*

There are a large variety of graphite powders commercially available. A preliminary study with a few different grades of flake graphite has led to the selection of Asbury 3775 which is described as surface-enhanced natural flake graphite, Fig. 1.<sup>14</sup> It has a nominal carbon content of 98% with 24 m<sup>2</sup>/g of surface area. Asbury 3775 has been expanded and milled from larger natural graphite flakes using a fluid energy milling technology to average dimensions of 5-10  $\mu$ m in plane and about 100 nm in thickness.

### *Epoxy Resin*

The epoxy resin used is a diglycidyl ether of bisphenol F (DGEBF) under the name of Epon 862 combined with a diethyltoluenediamine (DETDA) curing agent called Epicure-W. The mix ratio is maintained at 100:26.5 in favor of Epon 862.<sup>15</sup>

## **Nitric Acid Oxidation**

### *Processing*

Wet oxidation of GNPs is performed with a 67% nitric acid (HNO<sub>3</sub>) solution. GNPs are immersed in the nitric acid solution and heated to 100° C for 30 min. with a 200:1 volume ratio of nitric acid to graphite. The GNPs are washed in deionized water and separated out via centrifugation until pH becomes neutral. The nitric acid treated GNPs are then dried in a vacuum oven at 200°C for 24 h. The acid-treated (AT) GNPs are compared with the as-received (AR) GNPs in Fig. 1. No discernible differences are seen with the exception of somewhat cleaner appearance on the surfaces of AT GNPs.

Nanocomposites are fabricated using Epon 862 epoxy resin and Epicure-W curing agent. The desired amount of GNPs are mixed with Epon and Epicure (100:26.5 ratio), stirred first by hand, and then for 10 min. by a shear mixer. A high-power ultrasonic horn is used for 20 min. to



achieve a more uniform dispersion of GNPs in the epoxy resin. The well dispersed mixture of epoxy and GNPs is then poured into silicone rubber molds having appropriate geometries for different types of tests in conformance with the applicable ASTM (American Society for Testing and Materials) standards.

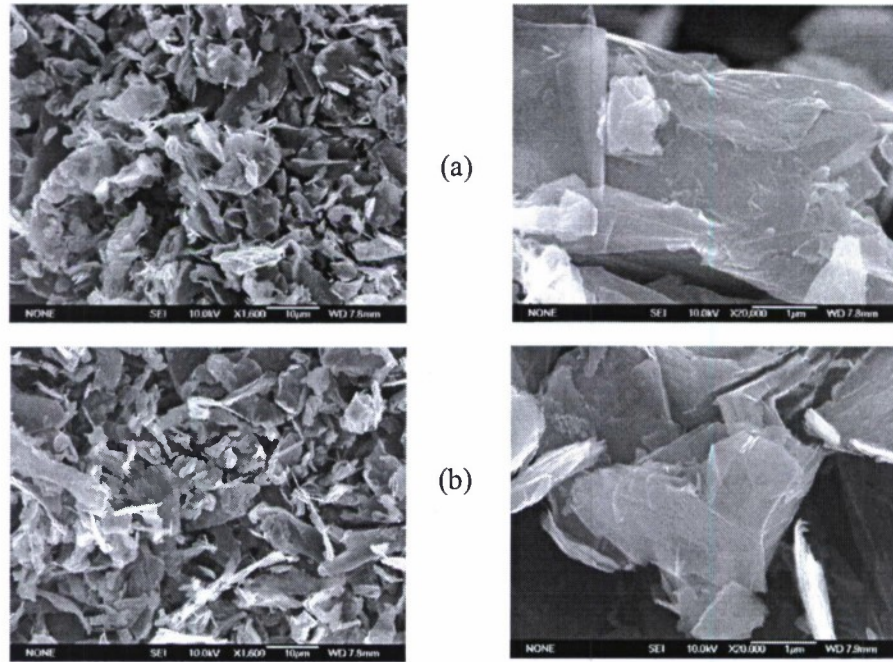


Fig. 1. Graphite Nanoplatelets (GNPs): (a) as received and (b) nitric acid treated for 30 min.

For comparison purposes, as-received GNPs are also used to fabricate the same type of specimens. These specimens provide the baseline data to show the effect of nitric acid treatment on nanocomposite properties.

#### *Tensile Properties*

Tensile properties have been measured using dog-bone shaped specimens having nominal dimensions of 1.2-mm thickness and 8.2-mm gage length in accordance with ASTM D-882. The test results are shown in Fig. 2 for both acid treated (AT) and as-received (AR) GNPs.

Regardless of the surface treatment, both strength and modulus increase with increasing GNP loading. The increases are rather rapid up to the GNP loading of 1 vol% and then slow down thereafter. The benefits of the acid treatment are obvious: the modulus and strength of the AT composite are much higher than those of the AR composite at each of the same GNP loadings. With addition of just 1 vol% of AT GNPs the composite can be made more than 70% stiffer than the resin. Without the acid treatment, however, the increase is much smaller. At the maximum particle loading of 4 vol% studied, the AT composite modulus is 6.4 GPa whereas the corresponding AR composite modulus is only 4.6 GPa.

The increase in strength shows the same trend as that in modulus. One major difference is that the strength does not increase much after 1 vol% GNP loading even for the AT composite. Furthermore, there is only a small strength increase for the AR composite: the maximum strength increase at 4 vol% is only 20% compared to 60% for the AT composite. The slowing down of strength increase for the AT composite is believed to be the difficulty of obtaining good GNP dispersion with increasing particle loading. The poor strength improvement in the AR composite is the result of poor interfacial bonding. However, the composite modulus is not as sensitive to the interfacial bonding as the strength is, and hence much higher increase in modulus is observed even for the AR composite.

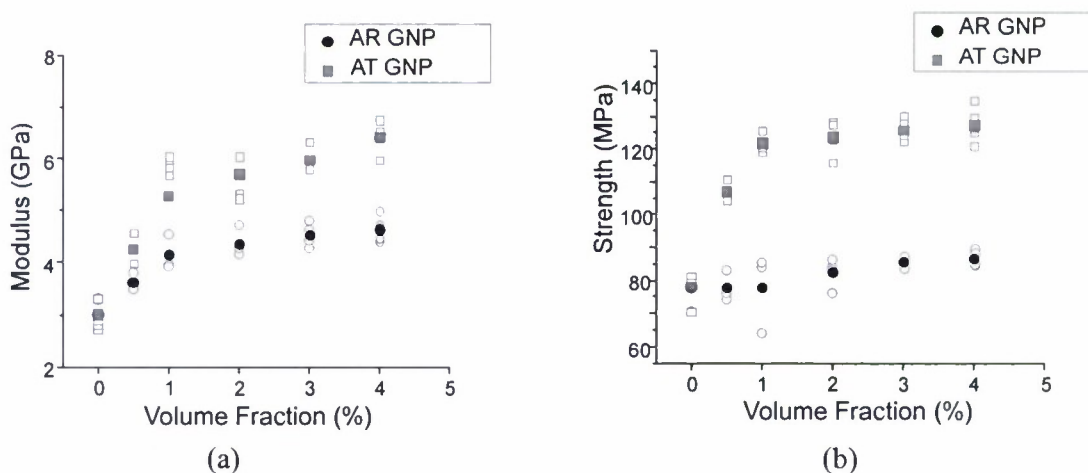


Fig. 2. Tensile properties of AR and AT GNP nanocomposites: (a) modulus and (b) strength.

Nitric acid treatment introduces carboxyl groups ( $-\text{COOH}$ ) on the GNP surface which can form an amide bonding with the amine curing agent. However, an excessive oxidation may damage the GNP surface. An optimum process is thus to produce the right amount of carboxyl groups without damaging GNPs. A carboxyl group can then react with an amino group on the curing agent to produce an ammonium carboxylate salt. Subsequent heating well above  $100^\circ\text{C}$  removes the water byproduct and yields an amide linkage:



The same reaction can occur under sonication without heating as the sonication can locally provide the necessary energy required for the reaction.<sup>16</sup>

Figure 3(a) shows that an optimum acid treatment time exists to yield optimum property improvement. For the amounts of materials used, the optimum treatment time appears to be 30 min. The FTIR spectra in Fig. 3(b) show the presence of the carboxyl group on the GNP surfaces.<sup>16,17,18</sup> The peaks are seen to grow with increasing treatment time up to 30 min. and

then remain almost the same thereafter.

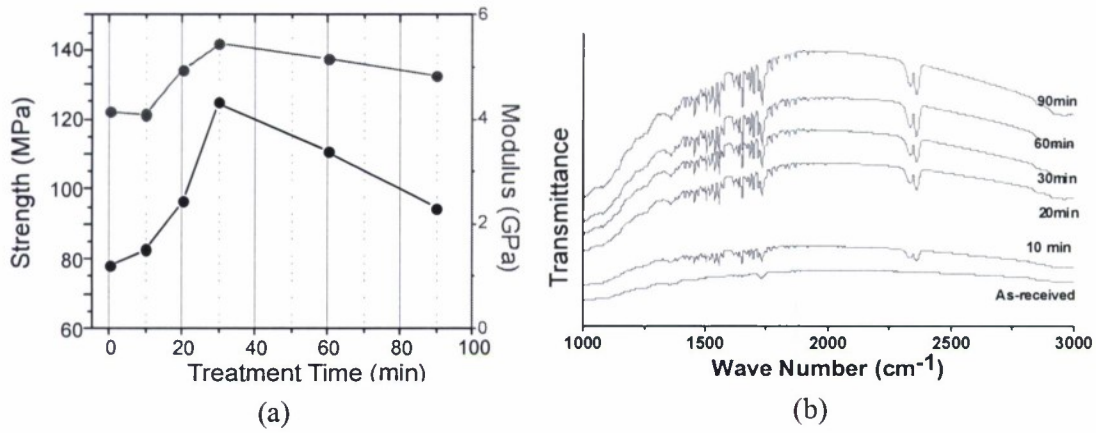


Fig. 3. Effects of nitric acid treatment time (1 vol% GNP): (a) tensile properties and (b) Fourier Transform Infrared (FTIR) spectra.

#### Compressive properties

Compressive properties have been measured using cylindrical specimens 12.7 mm in diameter and 40 mm long in accordance with ASTM D695-02. The GNP loading is fixed at 1 vol%. The compressive strength rather decreases, 14%, upon the addition of AR GNPs while it increases 23% when AT GNPs are used. AR GNPs appear to render the composite more brittle, as exhibited by failed specimens, Fig. 4. However, the AT composite retains the same ductility while exhibiting a higher strength.

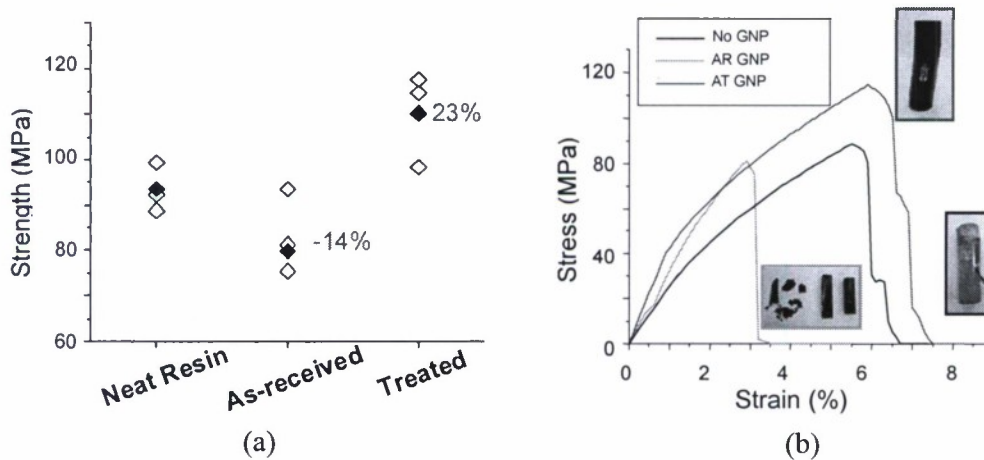


Fig. 4. Compressive properties (1 vol% GNP): (a) strengths and (b) stress-strain relations.



### Fracture Toughness

Fracture toughness has been measured following ASTM D5045 using single-edge-notch specimens in bending. The notch was introduced into the specimen and sharpened using a razor blade.

The AT composite shows a higher plane-strain fracture toughness  $K_{IC}$  than either of the neat resin and the AR composite, Fig. 5. However, the corresponding critical strain energy release rate  $G_{IC}$  calculated from  $K_{IC}$  is lower for the AT composite. The reason is that although  $K_{IC}$  is higher, so is the corresponding modulus and hence the resulting  $G_{IC}$  could be lower.

The fracture surface of the AR composite in Fig. 6 shows the imprint of a GNP that has been pulled out. However, there is no sign of any GNP debonding on the fracture surface of the AT composite. Although a poor interface may lead to a higher toughness especially in brittle matrix composites, e.g., ceramic matrix composites, such is not the case with epoxy matrix composites. A strong interface allows GNPs to resist crack propagation and can yield a higher toughness.

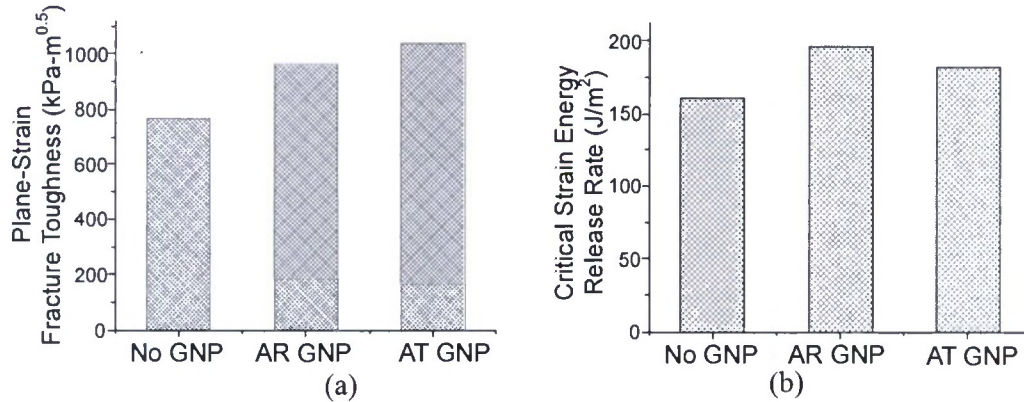


Fig. 5. Fracture properties (1 vol% GNP): (a) plane-strain fracture toughness and (b) critical energy release rate.

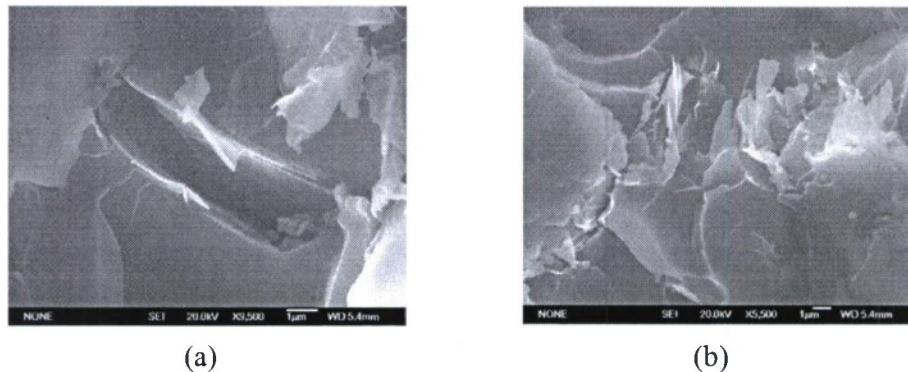


Fig. 6. Fracture surfaces (1 vol% GNP): (a) AR composite and (b) AT composite.

### Adhesive properties

Adhesive properties have been measured using single-lap joints with graphite/epoxy laminates as adherends in accordance with ASTM D3163-01. The adherend laminate has 8 layers of AS4 carbon fabric impregnated with Epon 862.

Two types of resins are used as adhesives: Epon 862 and a commercial epoxy glue based on a combination of bisphenol A-epichlorohydrin and a mercaptan curing agent. The commercial glue is included for comparison purposes.

As for compressive strength, the addition of AR GNPs does not improve the adhesive strength of Epon 862 although it is effective somewhat for the commercial glue, Fig. 7. However, the acid treatment increases the reinforcement effectiveness of GNPs for both adhesives. The improvement is much more for Epon 862 than for the commercial glue. The reason may be the amide bond that forms between the carboxyl group on the GNP surface and the amino group in the Epicure-W curing agent.

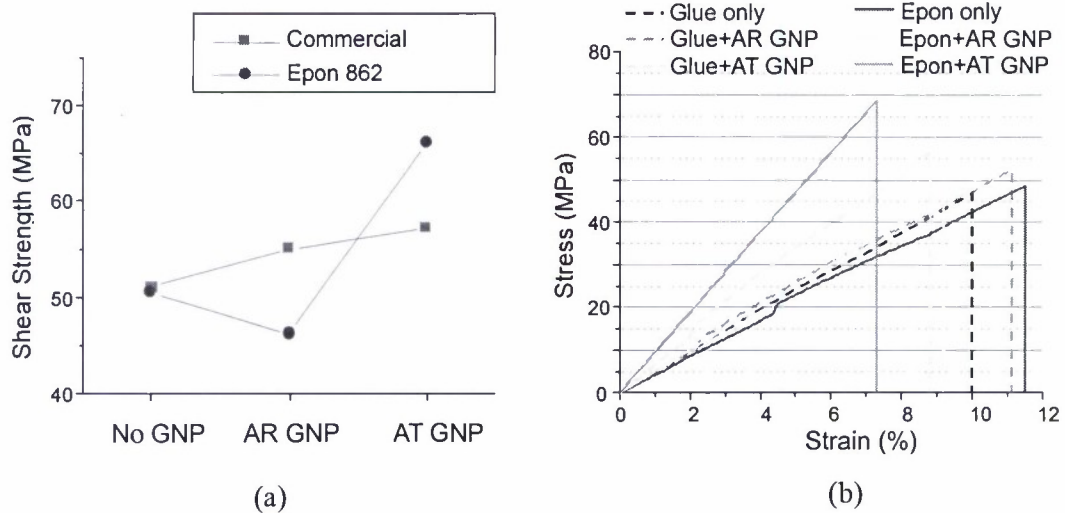


Fig. 7. Adhesive properties (1 vol% GNP): (a) single-lap shear strength and (b) stress-strain relations.

The higher composite modulus induced by the addition of AT GNPs manifests itself in a stiffer joint. Figure 7(b) plots the applied stress as a function of the average strain between grips. The AT GNP/Epon 862 composite shows the stiffest joint behavior followed by the AT GNP/commercial glue composite. AR GNPs do not appear to increase the joint stiffness significantly.

### Thermal Conductivity

The transient hot-wire method has been used to measure the thermal conductivity of the polymer nanocomposites.<sup>19</sup> Figure 8 shows the thermal conductivities of the neat resin and the two types of nanocomposites monotonically increasing with increasing temperature. This trend is typical of highly disordered dielectric materials. Compared with the neat resin, the improvement in thermal conductivity is approximately 2~3 % for the AR composite and 3~6% for the AT



composite. The modest improvement in thermal conductivity is rather surprising since the thermal conductivity of graphite ( $\sim 3000 \text{ W/m K}$ ) is orders of magnitude higher than that of the matrix resin. It appears that the large resistance to heat conduction across interfaces between GNPs and the polymer matrix strongly impedes heat conduction in the nanocomposites. Nevertheless, the stronger interfacial bonding enabled by the acid treatment leads to a slightly higher thermal conductivity.

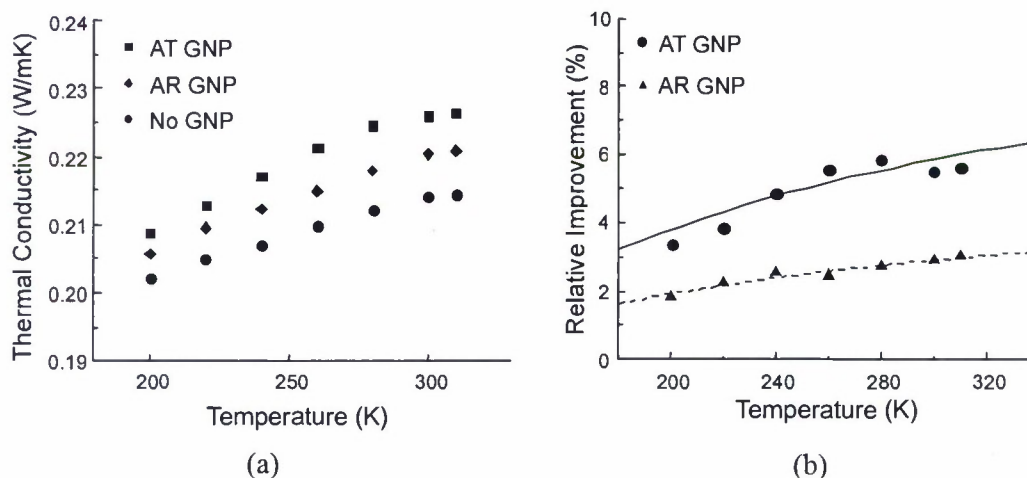


Fig. 8. Thermal conductivity (1 vol% GNP): (a) thermal conductivity increasing with temperature and (b) thermal conductivity improvement increasing with temperature.

### *Electrical and Dielectric Properties*

Similarly to thermal conductivity, electrical conductivity increases as more GNPs are added, Fig. 9. The increase in electrical conductivity accelerates with increasing GNP loading, which is contrary to the increase in strength. As more GNPs are added to the matrix, the chances of their coming into contact with one another increase and hence the resulting conductivity increases. The results in Fig. 9 show that AT GNPs yield higher composite conductivity than AR GNPs as the former allows for better interfacial bonding.

Figures 10 and 11 show the real and imaginary permittivities, respectively, of the nanocomposites<sup>20</sup>. Both permittivities increase with increasing GNP loading regardless of the surface treatment. Similar trends are observed for composites reinforced with carbon nanotubes and carbon blacks when the particle loading is low.<sup>21, 22, 23</sup>

A GNP/epoxy composite is a mixture of insulating regions and a conducting network. The electron conduction between conductive particles occurs via a combination of direct contact, electron tunneling through gaps and dielectric breakdown of the matrix in gaps. The effective scale of gaps is dependent on the electromagnetic frequency and is related to the distance of electron movement in the alternating electric field. The gaps that are smaller than electron displacements act as insulators and contribute to the real part of permittivity, i.e., the dielectric

constant of the composite. The remaining parts can be treated as part of the conducting network and contribute to the imaginary permittivity.

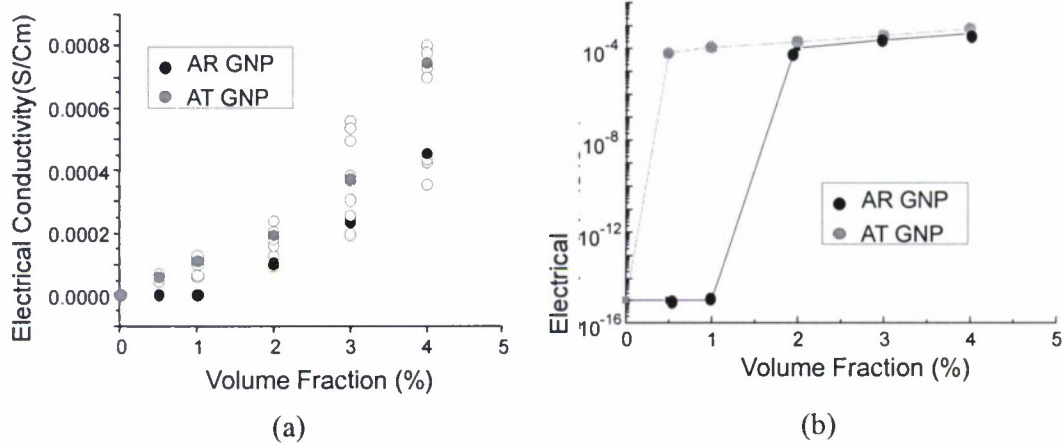


Fig. 9. Electrical conductivity: (a) absolute scale and (b) logarithmic scale.

Figure 10 shows the real permittivities of the composites increasing slightly after the additional nitric acid treatment. The surface treatment may reduce pores and unbonded interfaces between the conductive GNPs and the insulating epoxy, and remove contaminants from the GNP surfaces, thereby improving the real permittivity. Also, better dispersion in the AT GNP composite may facilitate the electrical isolation of individual GNPs. Contrary to the real permittivity, the imaginary permittivity shows little change after the nitric acid treatment, Fig. 11.

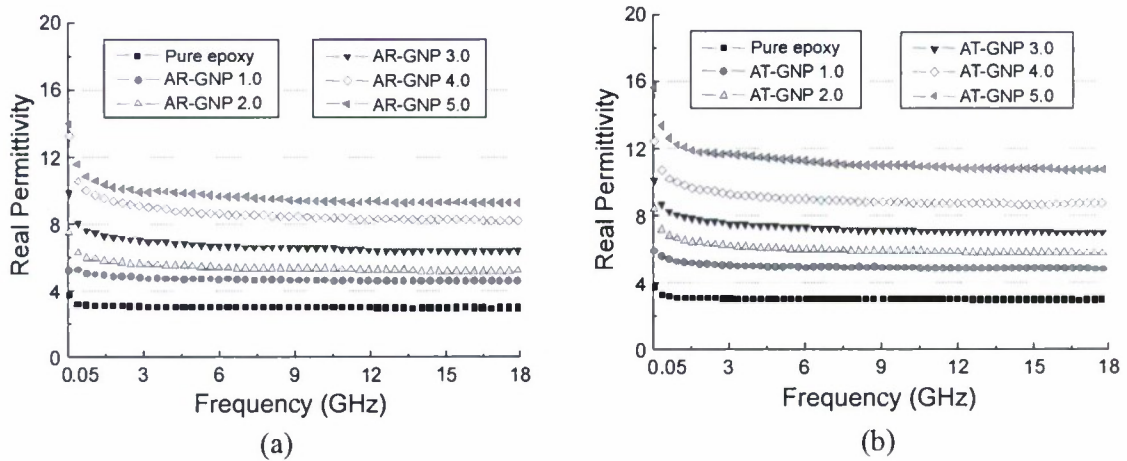


Fig. 10. Real permittivity: (a) AR composite and (b) AT composite

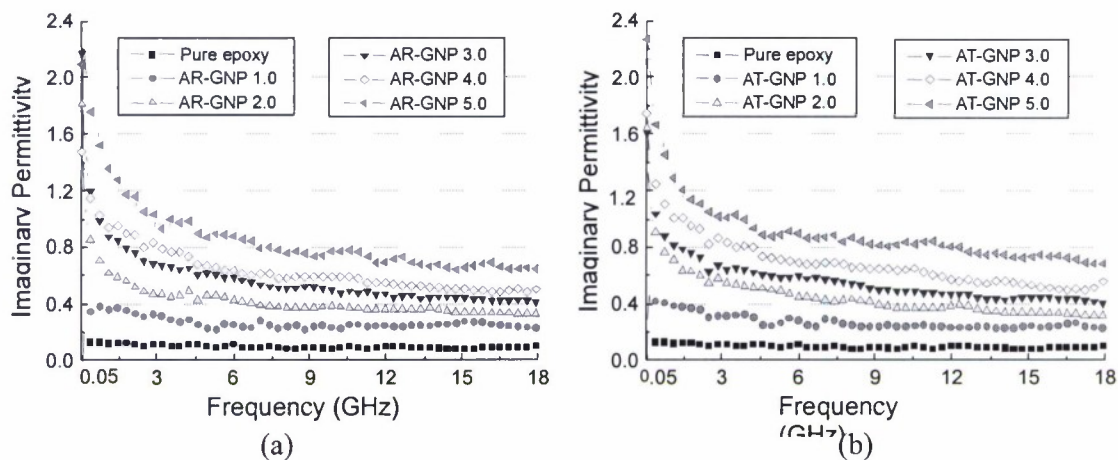


Fig. 11. Imaginary permittivity: (a) AR composite and (b) AT composite.

### Effect of GNP Dispersion

Sonication at an ultrasonic frequency is an effective means of achieving good dispersion of nanoparticles while promoting the formation of amide linkage between the carboxyl group and the amino group. However, it is not clear how much sonication is needed to yield optimum results. Therefore, two sets of experiments have been carried out to answer this question.

In the first set of experiments a mixture of AR GNPs, Epon 862 and Epicure W is sonicated in an ice bath using an ultrasonic horn for various periods of time. The mixture is then degassed, poured into molds and cured at 120° C for 4 h. In the second set of experiments, Epon 862 is left out during the initial sonication. It is later added to the mixture of AR GNPs dispersed in Epicure W. The final 3-component mixture is mechanically stirred briefly for 20 min. and then sonicated further for 30 min. The final cure procedure is the same as in the first set of experiments.

The quality of GNP dispersion as seen on an optical microscope is shown in Fig. 12 for the first experiments. After 6 h, there is no more discernible improvement in dispersion quality. Similar results are obtained for the second experiments.

The effect of sonication time on tensile strength is shown in Fig. 13(a) for the two sets of experiments. In both cases, the strength increases initially with increasing sonication time. However, after 4-6 hours, there is no more strength increase, indicating probably no further improvement in particle dispersion. In the first experiments where both Epon 862 and Epicure W are sonicated together, the local heating induced by sonication is large enough to cure the resin at the tip of the horn after 4 h of sonication. This is believed to explain a slight decrease in strength observed after thereafter. In the second set of experiments where only the curing agent is sonicated initially and Epon 862 is added later, there is no decrease in strength. Rather the strength increases slightly even after 4 h of sonication. Nevertheless, for the amount of materials used, the optimum sonication time is seen to be 6 h.



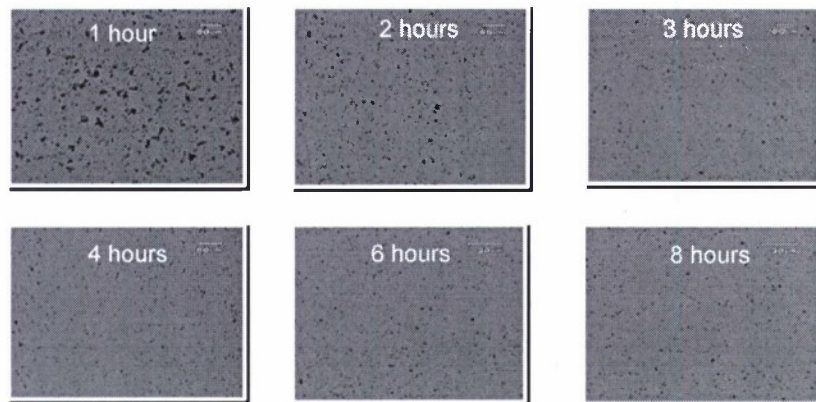


Fig. 12. GNP dispersion quality as a function of sonication time (0.25 vol% AR GNP in Epon and Epicure).

The effect of higher GNP loading on tensile strength is shown in Fig. 13(b) where a fixed sonication time of 6 h is used. The strength increase with GNP loading is asymptotic as in Fig. 2, with a maximum strength of almost 130 MPa reached at 4 vol%. It is interesting to note that this AR composite strength obtained after 6 h of sonication is almost the same as the AT composite strength which is realized with only 20 min. of sonication.

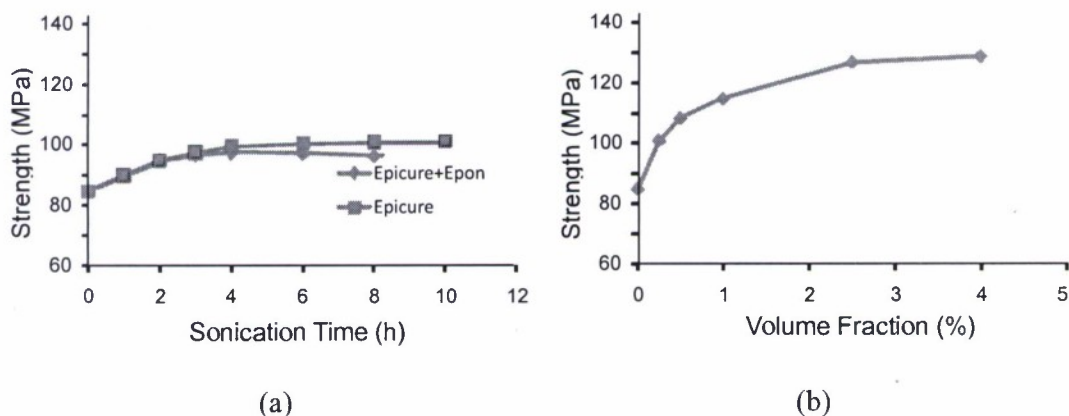


Fig. 13. Variation of tensile strength with (a) sonication time (0.25 vol% AR GNP) and (b) AR GNP loading (6-h sonication).

### Chemical Functionalization

Functional groups chemically bonded on graphite surfaces that are compatible with the matrix resin are expected to lead to improved interfacial bonding and hence higher composite

strength. The two types of functional groups chosen to study this effect are an epoxy-based group and an amine-based group, Fig. 14.<sup>23</sup> Both types have been synthesized and provided by Dr. Loon-Seng Tan's group at AFRL/RXBP.

Three different processes have been used to disperse the functionalized GNPs (f-GNPs) in the resin using an ultrasonic bath.<sup>24</sup> In process E (Epon first), f-GNPs are sonicated in Epon for 1 h. The curing agent is then added, mechanically stirred for 30 min. and finally sonicated again for 1 h. The final step is to degas, mold and cure at 120°C for 4 h. In process C (curing agent first), the sequence of adding Epon and Epicure is reversed while the rest of the steps remain the same.

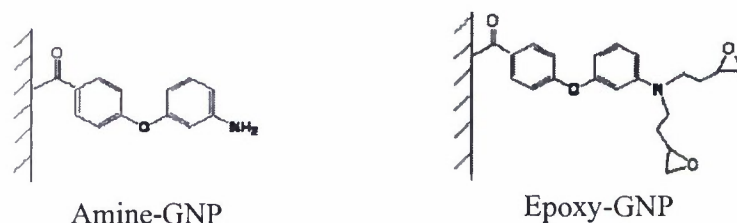


Fig. 14. Two types of chemical functionalization on GNP surface.

Optical micrographs of the mixtures before curing are shown in Fig. 15. It is clearly seen that the amine-GNPs yield a more uniform dispersion and higher strengths than the epoxy-GNPs in both processes E and C. The same trend is observed when Epicure is added before Epon: that is, process C yields better dispersion and higher strengths than process E. These results indicate that Epicure has more affinity to both types of GNPs and that amine-GNPs have better bonding to the matrix resin.

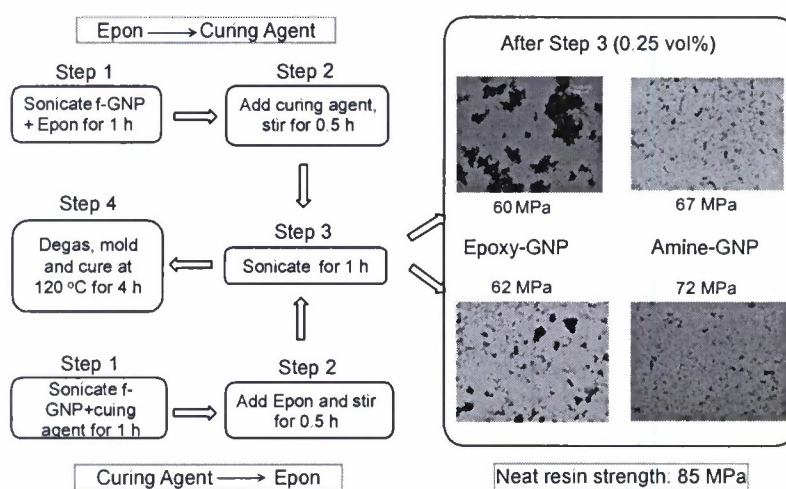


Fig. 15. Processes E and C for f-GNPs: amine-GNPs (right) and curing-agent-first mixing (bottom), respectively, showing better dispersion and higher strengths.

In order to improve the GNP dispersion, a mixed solvent consisting of ethanol and THF (tetrahydrofuran) in a 2:1 ratio has been used in the last process S (solvent), Fig. 16. This mixed solvent has been found to work well after a few trials. In this process, f-GNPs are sonicated in the mixed solvent for 3 h, followed by addition of Epicure and 3 h of sonication. In light of the better results from process C, Epicure is added first. One-fourth of the required Epon is then added, mechanically stirred for 30 min. and sonicated for 1 h. The solvent is evaporated in a vacuum oven, and the remaining Epon is added, mechanically stirred for 30 min. and finally sonicated for 1 h. The entire mixture is then cured following the same procedure as in the other processes.

Again, amine-GNPs show better dispersion and higher strength compared with epoxy-GNPs. Also, a better dispersion resulting from the use of the solvent appears to yield a higher strength, 90 MPa vs. 72 MPa. There is a clear correlation between the dispersion quality and the composite strength: a better dispersion yields a higher strength.

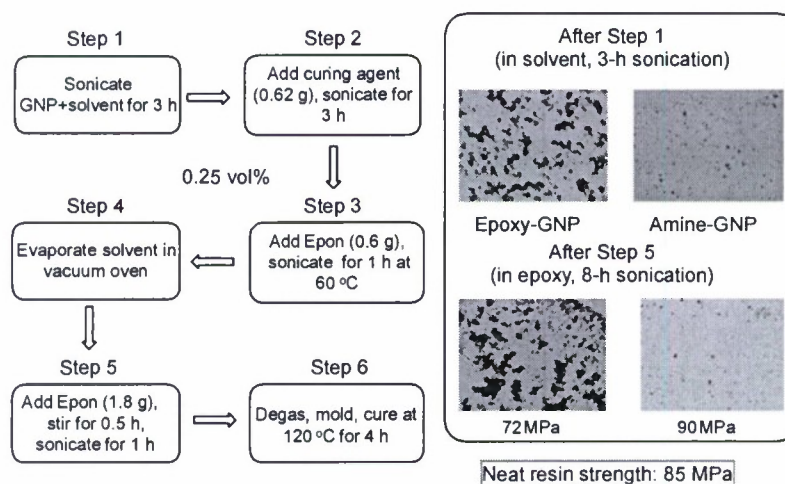


Fig. 16. Process S using a mixed solvent: amine-GNPs showing better dispersion and higher strengths.

Process S has been used to further study the effect of higher amine-GNP loading on the composite properties. The results show that further increase in strength with increasing particle loading is possible if the dispersion is good, Fig. 17.

### Intercalation, Expansion and Exfoliation

The reinforcement efficiency of GNPs depends on the aspect ratio so that thinner GNPs would be more desirable for the same planar dimension. Because of the layered nature of their microstructure, GNPs can be made thinner through intercalation, expansion and exfoliation. Much research has been done on intercalation of various elements into graphite.<sup>25, 26</sup> Improvements in strength, electrical conductivity and thermal conductivity are reported in the literature.<sup>27, 28, 29, 30</sup>



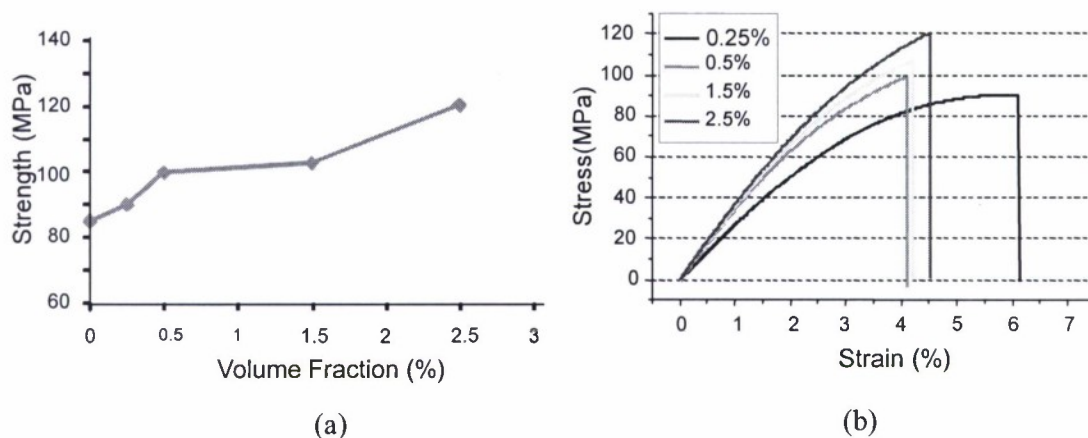


Fig. 17. Effect of amine-GNP loading on composite properties: (a) strength and (b) stress-strain relations

Potassium (K) has been intercalated into as-received GNPs to produce the first ( $KC_8$ ) and fourth ( $KC_{48}$ ) stage compounds using two different C/K stoichiometric ratios of 1.534 and 9.202, respectively.<sup>31, 32</sup> The first stage graphite intercalation compound (GIC) consists of graphite and potassium layers alternating with each other and appears gold. The fourth stage GIC with blue color has 4 graphite layers sandwiched between two potassium layers. For expansion, these two GICs are further reacted with dehydrated benzene to produce ternary GICs:  $KC_8$ -B and  $KC_{48}$ -B. The final treatment involves the usual nitric acid treatment. Scanning electron microscopy (SEM) micrographs of  $KC_{48}$ -B GICs are shown in Fig. 18. As with AR GNPs, no discernible differences are seen on the surfaces after the acid treatment.

The processing of composites using GICs is the same as for GNPs. The GICs exfoliate during this phase as a result of sonication and polymerization. Contrary to the expectation, however, the GICs do not appear to improve the composite strength much, Fig. 19. Rather, the effect of acid treatment is more conspicuous. The potassium intercalation definitely improves the electrical conductivity. This is believed to be due to the increased conductivity of potassium GICs themselves.<sup>33, 34</sup> Compared with untreated AR GNPs,  $KC_{48}$ -B GIC yields almost four times as high an electrical conductivity. The lower conductivity of  $KC_8$ -B composite is the result of  $KC_8$  having a lower conductivity than  $KC_{48}$ . The conductivity of K-GIC reaches a maximum around 5<sup>th</sup> stage and then increases as the stage number increases or decreases.<sup>34</sup>

### Potential Applications

With their ready availability, graphite nanoplatelets offer a cost-effective alternative to carbon nanotubes in many applications as they share almost the same properties. With a 2-dimensional structure, GNPs are more efficient as a reinforcement phase. Thus they can be used to reinforce polymers, ceramics and metals.

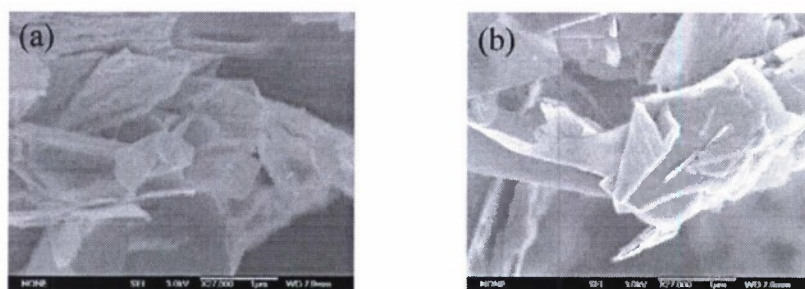


Fig. 18. SEM micrographs of  $KC_{48}$ -benzene graphite intercalation compound: (a) before acid treatment and (b) after acid treatment.

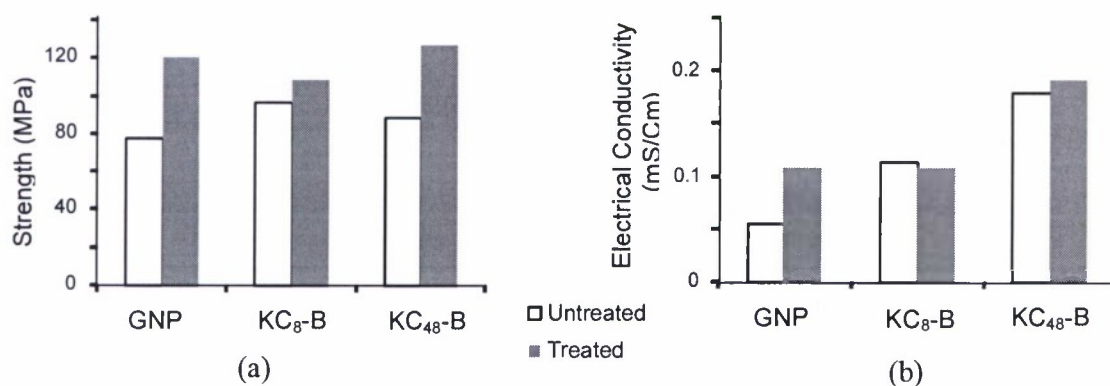


Fig. 19. Effects of intercalation (1 vol% GNP) on: (a) tensile strength and (b) electrical conductivity.

Their platelet geometry makes GNPs ideally suited for application in diffusion barrier films and coatings, similarly to organoclays. They are not photo reactive and can protect the matrix polymer from ultraviolet light. Their high electrical conductivity can be used to provide protection from electromagnetic interference.

Graphite fiber composites are finding ever increasing applications, as demonstrated by the new Boeing 787. GNPs can be added to the matrix of these composites to improve the matrix-controlled properties, such as matrix cracking. At present, the biggest advantage of GNPs is their cost effectiveness compared with carbon nanotubes.

## Conclusions

Graphite nanoplatelets possess many desirable properties such as those carbon nanotubes and fibers offer. Thus they can be used in many applications where a platelet geometry is needed or as a complement to carbon nanotubes and fibers. They are readily available and cost effective.

The key to the full utilization of GNP properties in composites is their uniform dispersion in and strong interfacial bond with the matrix. These are essentially the same requirements as for

carbon nanotubes. As much effort has been spent on meeting these requirements for carbon nanotubes, results of these efforts can no doubt be used to improve the properties of GNP composites.

When a proper grade of flake graphite (Asbury 3775) is used together with an epoxy (Epon 862 with Epicure W), the required processing to produce a good quality composite is rather simple. Oxidation of GNPs with nitric acid followed by their thorough dispersion via intense sonication can yield composites of high quality. The sonication appears to help the carboxyl group on the GNP surface react with the amino group on the curing agent to form an amide linkage. The best composite strength obtained this way is as high as 1.7 times the neat resin strength with just 1-vol% addition of acid treated GNPs. The corresponding electrical conductivity is about 0.1 mS/cm. Intercalation of potassium and benzene into GNPs can further increase the electrical conductivity.

Further improvements in composite properties appear possible when acid-treated GNPs are sonicated longer in the amine curing agent to allow the full formation of amide linkage. The GNP-coupled amine curing agent can then be used together with a base epoxy resin to fabricate GNP composites. However, further research is needed to find the optimum sonication time. Full exfoliation of GNPs followed by optimum acid treatment and sonication is another area of promising research to improve GNP composites. Also, it remains to be seen how the synergistic combination of acid treatment and intense sonication should be optimized for different grades of GNPs and other resins.

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### References

- <sup>1</sup> Y. Dzenis, Science 319, 419 (2008).
- <sup>2</sup> D.M. Riggs, R.J. Shuford, and R.W. Lewis, in Handbook of Composites, G. Lubin, Ed., Van Nostrand Reinhold, 196 (1982).
- <sup>3</sup> P. Delhaes, Ed., Graphite and Precursors, Gordon and Breach Science Pub. (2001).
- <sup>4</sup> O. Choi, S. Gilje, H.T. Hahn, and R.B. Kaner, Proc. SAMPE ISTC 37 (2006).
- <sup>5</sup> J. Li, J.-K. Kim, and M.L. Sham, Scripta Materialia 53, 235 (2005).
- <sup>6</sup> J. Li, M.L. Sham, J.-K. Kim, and G. Marom, Composites Science and Technology 67, 296 (2007).
- <sup>7</sup> L.T. Drzal and H. Fukushima, Proc. SAMPE (2003).
- <sup>8</sup> L.T. Drzal, and H. Fukushima, Proc. American Society for Composites 19th Technical Conference (2004).
- <sup>9</sup> R.A. Vaia and E.P. Giannelis, MRS Bulletin May, 394 (2001).
- <sup>10</sup> S.S. Ray and M. Okamoto, Progress in Polymer Science 28, 1539 (2003).
- <sup>11</sup> S. Banerjee, T. Hemraj-Benny, and S.S. Wong, Advanced Materials 17, 17 (2005).



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- <sup>12</sup> A. Hirsch, Angew. Chem. Int. Ed. 41, 1853 (2002).
- <sup>13</sup> P.V. Lakshminayaranan, H. Toghiani and C.W. Pittman, Carbon 42, 2433 (2004).
- <sup>14</sup> Asbury Carbons, [www.asbury.com](http://www.asbury.com).
- <sup>15</sup> Hexion Specialty Chemicals, <http://www.resins.com/resins/am/pdf/SC1183.pdf>.
- <sup>16</sup> T. Ramanathan, F. T. Fisher, R. S. Ruoff, and L. C. Brinson, Chem. Mater. 17, 1290 (2005).
- <sup>17</sup> H. Peng, L.B. Alemany, J.L. Margrave, and V.N. Khabashesku, J. Am. Chem. Soc. 125, 15174 (2003).
- <sup>18</sup> Y. Wang, Z. Iqbal and S.V. Malhotra, Chemical Physics Letters 402, 96 (2005).
- <sup>19</sup> M.T. Hung, M.T., Choi, O., Ju, Y.S., and Hahn, H.T., Applied Physics Letters 89, 023117 (2006).
- <sup>20</sup> S.E. Lee, O. Choi, and H.T. Hahn, Applied Physics Letters 104, 033705 (2008).
- <sup>21</sup> S.-E. Lee, J.-H., Kang and V.-G. Kim, Composite Structures 76, 397 (2006).
- <sup>22</sup> J.-H. Oh, K.-S. Oh, C.-G. Kim, and C.S. Hong, Composites Part B: Engineering 35, 49 (2004).
- <sup>23</sup> D.H. Wang, M.J. Arlen, J.-B. Baek, R.A. Vaia, and L.-S. Tan, Macromolecules 40, 6100 (2007).
- <sup>24</sup> Z. Wang, D.H. Wang, L.-S. Tan, and H.T. Hahn, unpublished work.
- <sup>25</sup> M.S. Dresselhaus and G. Dresselhaus, Advances in Physics 51, 1 (2002).
- <sup>26</sup> T. Enoki, M. Suzuki and M. Endo, Graphite Intercalation Compounds and Applications, Oxford University Press, 2003.
- <sup>27</sup> S. Stankovich, D.A. Dikin, D.H.B. Dommett, K.H. Kohlhaas, E.J. Zimney, E.A. Stach, R.D. Piner, S.T. Nguyen, and R.S. Ruoff, Nature 442, 282 (2006).
- <sup>28</sup> H. Fukushima, K. Kalaitzidou and L.T. Drzal, Proc. 16th International Conference on Composite Materials (2007).
- <sup>29</sup> A. Yu, P. Ramesh, M.E. Itkis, E. Bekyarova, and R.C. Haddon, R.C. Journal of Physical Chemistry C 111, 7565 (2007).
- <sup>30</sup> S. Stankovich, D.A. Dikin, G.H.B. Dommett, K.M. Kohlhaas, E.J. Zimney, E.A. Stach, R.D. Piner, S.T. Ngyuen, and R.A. Ruoff, Nature Letters 442, 282 (2006).
- <sup>31</sup> L.M. Viculis, J.J. Mack, O.M. Mayer, H.T. Hahn, and R.B. Kaner, Journal of Materials Chemistry 15, 974 (2005).
- <sup>32</sup> J.J. Mack, L.M. Viculis, A. Ali, R. Luoh, G. Yang, H.T. Hahn, F.K. Ko, and R.B. Kaner, Advanced Materials 17, 77 (2005).
- <sup>33</sup> E. McRae, D. Billaud, J.F. Mareche, and A. Herold, Physica B 99, 489 (1980).
- <sup>34</sup> H. Kim, H.T. Hahn, L.M. Viculis, S. Gilje, and R.B. Kaner, Carbon 47, 1578 (2007).